



(11) (A) No 1 241 572

(45) ISSUED 880906

(52) CLASS 117-158
C.R. CL. 204-22.6

(51) INT. CL. C23C 2/02⁴

(19) (CA) **CANADIAN PATENT** (12)

(54) Galvanizing Procedure and Galvanized Product Thereof

(72) Sakai, Daniel S.,
Canada

(73) Granted to Stelco Inc.
Canada

(21) APPLICATION No. 444,306

(22) FILED 831228

No. OF CLAIMS 18

Canada

DISTRIBUTED BY THE PATENT OFFICE, OTTAWA
CCA-274 (11-82)

BEST AVAILABLE COPY

444306

ABSTRACT OF THE DISCLOSURE

Ferrous alloy strip, wire, pipe or formed articles, is galvanized using hot dip in a molten zinc-aluminum bath. Enhanced corrosion resistance is achieved by precoating the ferrous alloy surface with a metal which is wettable by and reacts with the zinc-aluminum bath, preferably nickel. The nickel precoat is preferably formed by electroplating in line with the galvanizing step and enables cold line galvanizing to be used.

15

20

25

30

35

IMPROVED GALVANIZING PROCEDURE AND GALVANIZED
PRODUCT THEREOF

The present invention relates to the galvanizing of ferrous surfaces.

Hot-dip galvanizing of continuous coils of steel strip in a molten zinc bath has for years been a standard method of providing steel with a surface having both a pleasing appearance and a corrosion-resistant protective layer. The steel strip is first treated to remove oxide from the surface, so as to enable wetting of the surface by zinc to occur in the hot dip bath. Oxide removal has conventionally been effected by using elevated temperature reducing gas atmospheres, the so-called "hot" lines, or by using chemical treatment followed by protection with fluxes, usually zinc ammonium chloride, the so-called "cold" lines.

The conventional zinc coatings do not possess adequate corrosion resistance for some applications and attempts have been made to provide a surface having enhanced corrosion resistance. One such attempt resides in including significant amounts of aluminum, preferably along with small amounts of silicon, in the hot dip zinc bath. This procedure is the subject of a number of patents, including Canadian Patents Nos. 763,386, 802,844 and 899,729. As is set forth therein, the coating bath comprises about 25 to about 70% by weight of aluminum, greater than about 0.5% by weight of the aluminum content of silicon, less than about 0.6% by weight of lead and the balance zinc.

Although potentially leading to improved corrosion resistance, in practice the prior art process has not provided the expected results. In accelerated and atmospheric corrosion tests, there have been observed rust bleed onto the sheet surface and pitting of the sheet surface of commercial samples of products produced by the prior art process. Further, although Canadian Patent No. 899,729 emphasizes the necessity for a thin uniform interfacial alloy layer between the



ferrous substrate and the zinc-aluminum coating, a variable thickness interfacial alloy was observed in the above-noted commercial samples, varying from 0 to about 2 microns in thickness.

5 In addition to the observed corrosion problems, at the present time, the prior art process is limited to the treatment of steel strip on hot galvanizing lines, since the fluxes used on cold lines are unable to remove aluminum oxides, so that the aluminum component
10 of the hot dip bath does not adhere properly to the steel surface. Further, the prior art process is unsuitable for most wire coating operations which are almost exclusively galvanized by cold line techniques using fluxes.

15 It has now been surprisingly found that the application of a metallic precoat to the ferrous alloy surface prior to hot dip galvanizing in a molten zinc-aluminum bath leads to the provision of a galvanized surface of significantly-improved corrosion
20 resistance and which can be applied using cold-line techniques.

Accordingly, in an aspect of the present invention, there is provided an improvement in a method of coating a ferrous surface by contact with a molten
25 bath which contains about 25 to about 70% by weight of aluminum, silicon in an amount of at least about 0.5% by weight of the aluminum, and the balance by weight of zinc, except for any minor metal constituents. The improvement comprises forming an adherent thin coating
30 of a metal on the ferrous surface prior to contact with the molten bath, the metal being one which is wettable by and reacts with the components of the molten bath and which is selected from the group consisting of nickel, bismuth, antimony, manganese, cobalt, tin,
35 zinc, cadmium and copper.

The microstructure of the product which is obtained using the method of the present invention is significantly different from that obtained in the prior art. The microstructure comprises a ferrous alloy

substrate layer, a substantially uniform thickness intermetallic alloy layer, usually having a thickness of about 2 to about 4 microns, on the substrate layer and comprising an intermetallic alloy of iron, zinc,
5 aluminum, silicon and the precoat metal, preferably nickel, and an outer zinc-aluminum layer comprising an aluminum-rich phase immediately adjacent the intermetallic alloy layer and a continuous aluminum phase having zinc-rich aggregates and precoat
10 metal-rich aggregates dispersed therethrough.

Accordingly, in another aspect of the invention, there is provided a ferrous substrate having a ductile, adherent, corrosion resistant coating metallurgically bonded thereto through a continuous uniform thickness
15 intermetallic alloy layer comprising iron, aluminum, zinc, silicon and an interalloying metal which is selected from the group consisting of nickel, bismuth, antimony, manganese, cobalt, tin, zinc, cadmium and copper, the coating comprising about 25 to about 70% by
20 weight of aluminum, silicon in an amount of at least about 0.5% by weight of the aluminum and the balance by weight of zinc except for minor metal constituents and having a region rich in aluminum immediately adjacent the intermetallic alloy layer and aggregates of zinc
25 and aggregates of interalloying metal dispersed in a continuous phase of aluminum.

The process of the invention may be effected in a continuous on-line manner and also is applicable to the galvanizing of a wide variety of ferrous alloy
30 products, such as wire, pipe and preformed structural items, which have not heretofore been susceptible of galvanizing treatment by zinc-aluminum baths.

Accordingly, in a further embodiment of the invention, there is provided a continuous method for
35 the production of galvanized ferrous alloy strip, which comprises feeding ferrous alloy strip from a source thereof; subjecting the surfaces of the strip to cleaning operations to free the surfaces from contaminants; forming a thin adherent coating of a

metal on the cleaned surfaces of the ferrous alloy strip, the metal being one which may be rapidly applied to the surfaces, is capable of being rapidly wetted by and reacting with a zinc-aluminum alloy galvanizing bath, prevents iron oxidation, and its oxide is capable of being readily reduced by contact with the zinc-aluminum alloy galvanizing bath, the metal being selected from the group consisting of nickel, bismuth, antimony, manganese, cobalt, tin, zinc, cadmium and copper; preheating the coated ferrous alloy strip to a temperature of about 400° to about 700°F; passing the preheated coated ferrous alloy strip into contact with a zinc-aluminum alloy galvanizing bath having a temperature of about 1150° to about 1200°F to effect reaction and coating formation thereon, the galvanizing bath containing from about 25 to about 70% by weight of aluminum, silicon in an amount of at least about 0.5% by weight of the aluminum, and the balance by weight of zinc, except for minor metal constituents; controlling the thickness of the zinc-aluminum coating formed on the ferrous alloy strip; and cooling the zinc-aluminum coated strip at a rate of about 50° to 75°F/sec. at least until the temperature is below about 700°F.

Precoating of the ferrous alloy surface in this invention may be effected in any convenient manner, preferably by plating, most preferably by electroplating. The precoat metal may be any convenient metal which will be wetted by and react rapidly with the zinc-aluminum alloy melt, will prevent oxidation of the metal surface after it has been cleaned and its oxide is readily reduced by contact with the zinc-aluminum melt.

The invention is described further, by way of illustration, with reference to the accompanying drawings, in which:

Figure 1 is a schematic flow sheet of a continuous galvanizing line modified in accordance with one embodiment of the invention;

Figure 2 is a photomicrograph of a steel sheet coated in accordance with the present invention; and

Figures 3A to 3C are photomicrographs of a steel sheet coated in accordance with the invention at various stages of a Kesternich corrosion test(DIN 50018).

Referring to Figure 1, in a hot dip galvanizing line 10, steel strip 12 to be treated is unrolled from a coil 14 and first passes through a cleaning tank 16 which contains an alkaline solution to remove dirt from the surfaces of the strip 12. After a cold water rinse in a rinser 18, the steel strip 12 then passes into a pickling tank 20. The pickling tank contains acid to remove oxides from the steel strip surfaces. In conventional cold line operations hydrochloric acid is usually used, but in this invention sulfuric acid usually is used, so as to provide common anionic species with the anion present in the plating bath, described below. The pickled strip is rinsed in a rinser 22.

In conventional cold line operation, the steel strip 12, now free from surface contaminants, is provided with a flux coating. In accordance with the present invention, the fluxing step is omitted and, instead, the cleaned steel strip 12 passes into a plating tank 24, wherein the surfaces of the steel strip have a thin precoat metal layer applied thereto. Preferably, the coating is applied by electroplating, since this technique rapidly and efficiently forms a thin adherent metal coating on the surfaces of the steel strip. An alternative process which may be employed is by electroless plating.

In addition, since the precoating preferably is effected in line with the galvanizing, as illustrated, the metal must be such that it can be applied rapidly in a continuous mode. It is possible to effect the precoating as a separate operation but this procedure is less preferred.

B

Metals which are used to provide the precoat are nickel, bismuth, antimony, manganese, cobalt, tin, zinc, cadmium and copper, with nickel and tin being preferred, nickel being most preferred. Electroplating of the steel strip using these metals can be accomplished in less than about 5 seconds, typically less than about 1 second using conventional electroplating current densities of about 200 to about 300 amps/sq.ft. Coating thicknesses of at least about 0.05 microns are obtained by the electroplating treatment, the actual thickness depending on the coating conditions.

The electroplated steel strip resulting from the plating tank 24 is subjected to a cold water rinse in rinser 26 before passing to a preheater 28 wherein the temperature of the steel strip 12 is raised, usually to about 400° to about 700°F. The preheater 28 may be omitted, if desired, although it is preferred to utilize the same so as to decrease the thermal load on the galvanizing tank. When the preheating is effected, the metal chosen for the precoating must be one which will not reflow at the preheater temperature.

The preheated steel strip next enters a galvanizing tank 30 containing a molten galvanizing bath which essentially contains zinc, aluminum and silicon. The aluminum content of the tank may vary from about 25 to about 70% by weight while the silicon content is greater than about 0.5% by weight, usually up to about 3% by weight, with the balance being zinc, with the exception of minor metal constituents. It is preferred that the lead content of the bath not exceed about 0.6% by weight. One particular bath composition which has been utilized consists of about 55% by weight of aluminum, 43.4% by weight of zinc and about 1.6% by weight of silicon.

The temperature of the galvanizing bath in the tank 30 is considerably above conventional pure zinc galvanizing temperatures (about 850°F) and usually is about 1150° to about 1200°F, preferably about 1160° to

about 1180°F. These temperatures are higher than normally used in the prior art process using a zinc-aluminum galvanizing bath (about 1100° to about 1120°F). The contact time of the steel strip with the galvanizing bath is usually about 3 to about 5 seconds. The thickness of the coating provided on the steel strip is controlled in conventional manner, by wiping using air knives at the exit from the galvanizing tank 30. Any desired thickness may be provided on the steel strip surface, but it is preferred to provide a thickness of at least 25 microns.

The galvanized steel sheet resulting from the galvanizing tank 30 next passes upwardly through a cooler 32 wherein the steel strip is cooled by flowing air to solidify the zinc-aluminum metal coating. The rate of cooling of the strip must be controlled in order to develop the desired microstructure in the zinc-aluminum coating and usually is in the range of about 50° to about 75°F/sec. The cooling in the cooler 32 is effected to result in a steel strip leaving the cooler having a temperature of no more than about 700°F.

Further cooling then may be effected under ambient conditions. The cooled steel strip 12 next usually is passed over levelling rollers 34 and through a passivation tank 36 wherein it is treated with a passivation chemical, before finally to a wind-up roll 38.

The procedure described with respect to Figure 1 is effected continuously on steel strip to form galvanized sheet having a zinc-aluminum coating on both surfaces. If desired, the steel sheet may be galvanized on only one surface, using techniques known in the art. The speed of operation of the line may be any convenient value, for example, about 250 ft/min.

Precoating of the steel strip with nickel or other metal enables a zinc-aluminum coating to be applied to the steel strip in cold-line operation and the use of fluxes to be omitted. The operation also may be

carried out on any other ferrous alloy product, such as, wire, pipe and preformed structural items. The process is not limited to a cold-line operation and may be used to advantage on a hot-line operation.

5 The invention is illustrated further by the following Example:

Example:

Cold-rolled steel panels sizes 6 x 3 x 0.024 inch were alkali cleaned using the alkali cleaner sold under
10 the trademark "Pennsalt 74" for 10 seconds at 180°F. After a cold water rinse, the panels were pickled in 3% sulphuric acid at room temperature for 10 seconds, and given a further cold water rinse.

The panels were electroplated at room temperature
15 with nickel using a nickel anode in an electroplating bath composition comprising:

| | |
|---|---------|
| $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ | 240 gpl |
| $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ | 40 gpl |
| Boric acid | 30 gpl |

20 at an energy level of 150 coulombs/sq.ft. The plated panels were given a cold water rinse and dried.

The plated panels were dipped for 5 seconds in a galvanizing bath comprising, by weight, 55% aluminum, 43.5% zinc and 1.5% silicon and having a temperature of
25 1200°F. After withdrawal of the plates, the zinc-aluminum coating was cooled at a rate of about 70°F/sec.

The galvanized panels had a bright, spangled appearance, having a spangle size of about 0.5 to 1.0
30 mm. The panels had coating thicknesses varying from 0.7 to 1.2 mils. One sample was cross-sectioned and a photomicrograph of the cross-section was taken, and appears, at a magnification of 500x, as Figure 2. As may be seen, there is a lower steel substrate, an
35 uniform continuous intermetallic alloy layer on the substrate estimated as having a thickness of 2 to 4 microns, and an aluminum-zinc layer on top of the intermetallic alloy layer. The aluminum forms a substantially continuous phase while the zinc, showing

up as the darker areas, forms aggregates which are distributed within the aluminum phase. It will also be seen that the region immediately adjacent the intermetallic alloy layer is substantially free from zinc.

The panels were examined at 30 times magnification with a stereo microscope and no holes or other coating discontinuities were observed. Panels were reverse impacted (80 in-lb) and given a tight 90° brake bend. No flaking was observed. The same panels were then exposed to 92% relative humidity and 80°C for 16 days. Adhesion of the coating was maintained in the deformed locations. The panels were again impacted (80 in-lb) and flaking was still not observed. As a result of these tests, it was concluded that adhesion of the zinc-aluminum coating to the steel substrate was satisfactory and that the intermetallic alloy-coating interface was electrochemically stable.

Corrosion properties of the panels were tested ("Stelco") and compared with commercial samples of zinc-aluminum coated panels obtained from two commercial sources ("C.S.-A" and "C.S.-B").

(a) Electrochemical Properties:

Corrosion currents were measured on 1 cm² samples in aerated electrolytes by the linear polarization technique and the average of three tests were determined. All surfaces were finely polished prior to testing to remove any surface passivation. Galvanic capacity was estimated by coupling with steel and measuring the time, normalized against thickness, for the corrosion potential to exceed -0.775 volts vs. SCE. The results obtained are set forth in the following Table I:

TABLE I

| | Corrosion Current | | Galvanic Capacity |
|----------|---------------------------------------|------------|---------------------------------------|
| | ua/cm ² | | (secs) |
| | 2%Na ₂ SO ₄ pH4 | 3%NaCl pH2 | 2%Na ₂ SO ₄ pH2 |
| 5 Stelco | 110 | 268 | 2208 |
| C.S.-A | 192 | 680 | 1470 |
| C.S.-B | 158 | 550 | 920 |

It will be seen from the results set forth in Table I that the panels produced in accordance with the present invention had lower corrosion rates in both sulfate and chloride electrolytes than both the commercial samples and had superior galvanic capacity to both the commercial samples.

(b) Salt spray test:

Unpassivated Stelco samples and passivated commercial samples were subjected to the standard accelerated corrosion salt spray test for 750 hours. White rust formed on the panels produced in accordance with this invention after a short period of exposure, probably due to the unpassivated nature of the surface. However, after 750 hours, the Stelco samples were substantially free from red rust, whereas both the commercial samples exhibited substantial rust formation, the C.S.-B sample somewhat less so than the C.S.-A sample. These results demonstrate the improved barrier protection afforded by the process of the invention.

(c) Condensing SO₂ test:

Unpassivated Stelco samples and passivated commercial samples were subjected to the conventional condensing SO₂ test for 4 and 8 cycles. Minimal rust bleed at the sheared edge was exhibited by the samples produced in accordance with this invention, while considerable rust bleed was exhibited by the commercial samples, with less rust bleed being exhibited by the C.S.-B sample.

Figures 3A to 3C are photomicrographs of Stelco samples subjected to the condensing SO₂ test. Figure 3A is a photograph at 200 times magnification of the

sample after 4 cycles exposure. As would be expected, acid attack proceeded through the zinc rich phase but the corroding path, for the most part, did not continue to the intermetallic alloy layer. In the isolated instances when this penetration did occur, corrosion did not propagate along the interface, as can be seen in the 500 times magnification micrograph of Figure 3B. Little change occurred in the corrosion pattern after an additional four cycles, as can be seen from the 500x micrograph of Figure 3C taken at the end of that period.

It is considered that penetration to the alloy layer did not occur in the Stelco samples due to the presence of the aluminum-enriched zone adjacent to the alloy layer.

In summary of this disclosure, the present invention relates to an improved method of producing corrosion resistant galvanized surfaces using zinc-aluminum coating compositions, by precoating the ferrous alloy substrate. The microstructure of the coating which results is unique and leads to the enhanced corrosion resistance. Modifications are possible within the scope of this invention.

25

30

35

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. In a method of coating a ferrous surface by contact with a molten bath which contains about 25 to about 70% by weight of aluminum, silicon in an amount of at least about 0.5% by weight of the aluminum, and the balance by weight of zinc, except for any minor metal constituents, the improvement which comprises forming an adherent thin coating of a metal on said ferrous surface prior to said contact with said molten bath, said metal being one which is wettable by and reacts with the components of said molten bath and which is selected from the group consisting of nickel, bismuth, antimony, manganese, cobalt, tin, zinc, cadmium and copper.
2. The method of claim 1 wherein said metal coating is applied by plating.
3. The method of claim 2 wherein said plating is effected by electroplating.
4. The method of claim 1, 2 or 3 wherein said coating has a minimum thickness of about 0.05 micron.
5. The method of claim 1 wherein said metal is selected from the group consisting of nickel and tin.
6. The method of claim 1 wherein said metal is nickel having a minimum coating thickness of about 0.05 micron.
7. The method of claim 6 wherein said nickel is deposited by electroplating.
8. A continuous method for the production of galvanized ferrous alloy strip, which comprises:
 - feeding ferrous alloy strip from a source thereof,
 - subjecting the surfaces of said strip to cleaning operations to free said surfaces from contaminants,
 - forming a thin adherent coating of a metal on the cleaned surfaces of the ferrous alloy strip, said metal being one which may be rapidly applied to the surfaces, is capable of being rapidly wetted by and reacting with a zinc-aluminum alloy galvanizing bath, prevents iron

oxidation, and its oxide is capable of being readily reduced by contact with the zinc-aluminum alloy galvanizing bath, said metal being selected from the group consisting of nickel, bismuth, antimony, manganese, cobalt, tin, zinc, cadmium and copper,

preheating the coated ferrous alloy strip to a temperature of about 400° to about 700°F,

passing the preheated coated ferrous alloy strip into contact with a zinc-aluminum alloy galvanizing bath having a temperature of about 1150° to about 1200°F to effect reaction and coating formation thereon, said galvanizing bath containing from about 25 to about 70% by weight of aluminum, silicon in an amount of at least about 0.5% by weight of the aluminum, and the balance by weight of zinc, except for minor metal constituents,

controlling the thickness of the zinc-aluminum coating formed on the ferrous alloy strip, and

cooling said zinc-aluminum coated strip at a rate of about 50° to 75°F/sec. at least until the temperature is below about 700°F.

9. The method of claim 8 including subjecting the zinc-aluminum coated surfaces of the cooled ferrous alloy strip to a levelling procedure.

10. The method of claim 8 or 9 including passivating the zinc-aluminum coated surfaces of the cooled ferrous alloy strip.

11. The method of claim 8, wherein the thin adherent metal coating is formed by electroplating a coating of a minimum thickness about 0.05 micron in less than 5 seconds.

12. The method of claim 11 wherein said metal is nickel.

13. The method of claim 11 wherein said zinc-aluminum galvanizing bath contains about 55% by weight of aluminum, about 43.4% by weight of zinc and about 1.6% by weight of silicon.

14. The method of claim 11, 12 or 13 wherein said galvanizing bath has a temperature of about 1160° to about 1180°F.

15. The method of claim 11, 12 or 13 wherein the contact time of said ferrous alloy strip in said zinc-aluminum galvanizing bath is about 3 to about 5 seconds.

16. A ferrous substrate having a ductile, adherent, corrosion resistant coating metallurgically bonded thereto through a continuous uniform thickness intermetallic alloy layer comprising iron, aluminum, zinc, silicon and an interalloying metal which is selected from the group consisting of nickel, bismuth, antimony, manganese, cobalt, tin, zinc, cadmium and copper, said coating comprising about 25 to about 70% by weight of aluminum, silicon in an amount of at least about 0.5% by weight of the aluminum and the balance by weight of zinc except for minor metal constituents and having a region rich in aluminum immediately adjacent said intermetallic alloy layer and aggregates of zinc and aggregates of interalloying metal dispersed in a continuous phase of aluminum.

17. The product of claim 16 wherein said interalloying metal is selected from the group consisting of nickel and tin.

18. The product of claim 16 wherein said interalloying metal is nickel.



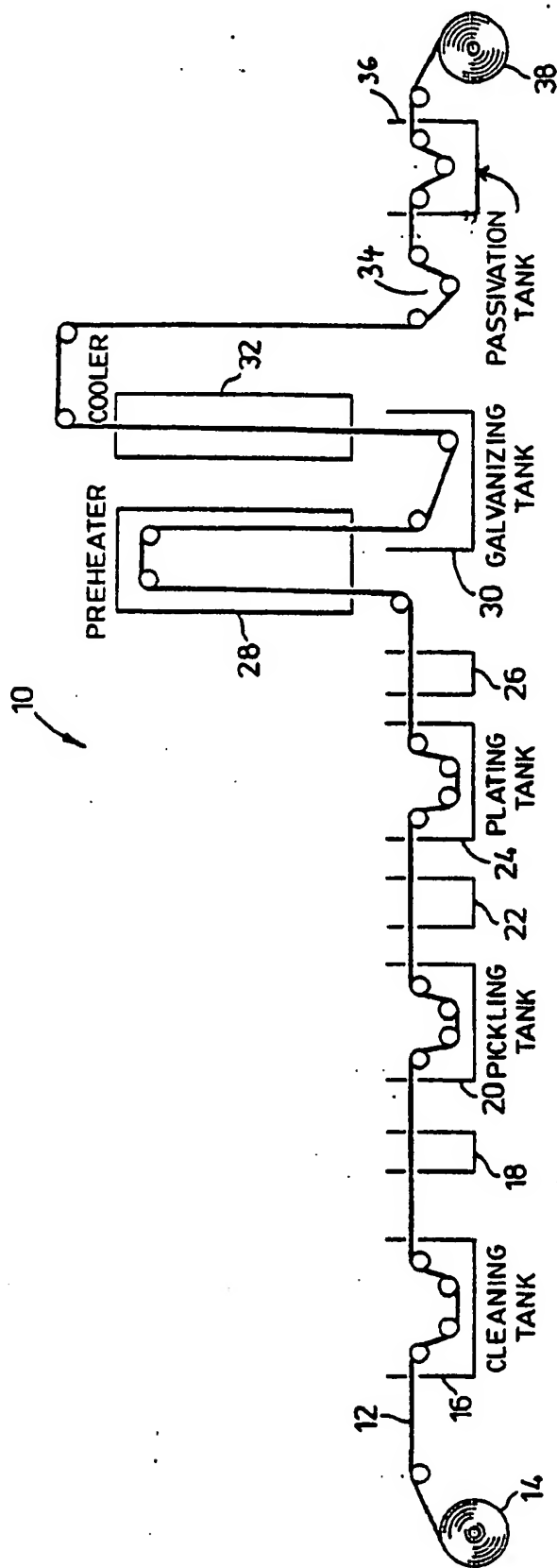


FIG. 1

Sim: M. L. Lanning

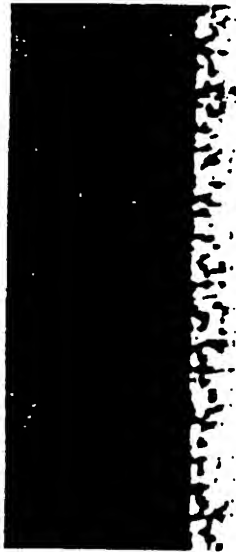


FIG. 3A



FIG. 3C



FIG. 2



FIG. 3B

Sum: 1/2. 1/2

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.